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TECHNICAL MEMORANDUM

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Waste Management & Cleanup Division
Department of Environmental Quality

To: Bill Dana, (DEQ)

From: John Montgomery, (E & E)

Subject: McCormick and Baxter, Task Order No. 88-97-5; Evaluation of Innovative Technologies for Enhanced (NAPL) Extraction.

Date: November 11, 1999

cc: David Anderson, DEQ
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1. Introduction and Purpose

Ecology and Environment, Inc. (E & E) has prepared this technical memorandum to discuss and evaluate innovative technologies for enhanced nonaqueous phase liquid (NAPL) extraction at the McCormick & Baxter (M&B) Company site in Portland, Oregon.

The purpose of this memorandum is to provide insight into the most accepted innovative technologies for NAPL removal from soil and groundwater.

The evaluation of innovative technologies is based on two general criteria: effectiveness and implementability at the M&B site. Most of the technologies described in this memorandum have been implemented as pilot-scale studies at other sites. Available costs associated with the innovative technologies are in Table 1.

2. Enhanced Nonaqueous Phase Liquid Recovery Technologies

Most of the technologies described in this memorandum are in situ technologies for soil and groundwater. Ex situ technologies have been researched but have limited scope in this memorandum because of the cost associated with soil and/or groundwater extraction and treatment.

Although much progress has been made recently in developing and improving cleanup technologies, there is still no proven technology for the restoration of denser-than-water nonaqueous phase liquid (DNAPL) source zones. The difficulty of this challenge is unprecedented in the field of groundwater engineering. Despite recent notable progress, the technologies available for the removal of DNAPL from the groundwater zone at appreciable rates are still experimental, and no DNAPL source zone of significant size has been fully restored using any of them (Pankow and Cherry, 1996). It is also a well-recognized fact that lack of credible performance and cost data limits the development of new technologies.

Table 1 provides a list of innovative technologies that have been identified by E & E in a search of various documents, reference texts, and Internet web-sites. These technologies employ various techniques that involve in situ and ex situ treatment of contaminants. Hydrous pyrolysis oxidation (HPO) has produced excellent results and has been applied at creosote sites. Six-phase soil heating is another successful technology that, because of possible implementation at a DEQ Voluntary Cleanup site, could be a candidate for a pilot-scale study. Dynamic underground stripping (DUS) could be the most versatile option because it utilizes a variety of techniques in conjunction with hydrous pyrolysis oxidation. Installation of a vertical barrier would aid in the efficiency of all technologies as long as the barrier material is compatible with the techniques applied to the soil. The following technologies are viable candidates for a pilot-scale study at the M&B site.

2.1 Six-Phase Soil Heating

2.1.1 Methodology

Scientists at the United States Department of Energy's (DOE's) Pacific Northwest Laboratories developed several innovative electrical technologies for soil and groundwater contamination. One of the technologies developed was six-phase heating.

Six-phase heating is a polyphase electrical technology that uses in situ resistive heating and steam stripping to accomplish subsurface remediation. A voltage control transformer converts conventional three-phase electricity into six electrical phases. These electrical phases then are delivered to the subsurface by vertical, angled or horizontal electrodes installed using standard drilling techniques.

Because the six-phase heating electrodes are electrically out of phase with each other, electrical current flows from each electrode to all of the other out-of-phase electrodes adjacent to it. It is the resistance of the subsurface to this current movement that causes heating. The result is a uniquely uniform subsurface heating pattern that can be generated in the saturated zones or in the vadose (unsaturated) zones.

Electricity takes the path of least resistance when moving between electrodes, and these pathways are heated preferentially. Examples of low resistance pathways include silt or clay lenses–horizontal deposits of sediment that are thin or discontinuous–and areas of high free ion content. As chlorinated compounds sink through the lithology, they become trapped on these silt and clay lenses. Over time, trapped solvents undergo biological dehalogenation, producing daughter compounds and free chloride ions. Thus, at DNAPL sites, the most impacted portions of the subsurface are also low resistance electrical pathways that are preferentially treated by six-phase heating.

By increasing subsurface temperatures to the boiling point of water, six-phase heating speeds the removal of contaminants by increased volatilization and in situ steam stripping. As subsurface temperatures climb, contaminant vapor pressure and the corresponding rate of contaminant extraction increase. The Henry's Law constant of vapor phase concentrations to dissolved phase concentrations increases by 15 times to 20 times as temperatures rise from 10° Celsius to 100° C. Direct in situ volatilization is an extremely important six-phase heating remediation mechanism for contaminants with boiling points below that of water.

The ability to produce steam in situ represents the second most signficant mechanism for contaminant removal using six-phase heating. Through preferential heating, six-phase heating creates steam from within the silt and clay stringers or lenses. The physical action of steam escaping from these tight soil lenses drives contaminants out of these otherwise diffusion-limited portions of the soil matrix, which tends to lock in contamination via low permeability of capillary forces.

The released steam then acts as a carrier for gas that, as it moves toward the surface, strips contaminants from groundwater and more permeable portions of the soil matrix. The presence of the steam also causes the boiling point of the DNAPL to become depressed, because of the partial pressure effects described by Dalton's Law of partial pressure.

Once in the vadose zone, rising steam and contaminant vapors are collected by conventional soil vapor extraction wells. A condenser then separates the mixture into condensate-laden vapor.

2.1.2 Evaluation of Six-Phase Soil Heating

This technology is effective at steam creation and subsequent vapor extraction. It is one of the more cost-effective steam technologies because steam is generated in situ by electrical phase heating of subsurface soil moisture. Electrical power for the heating array is supplied by a mobile power plant. The technology has been very effective at removing volatile organic compounds (VOC) contamination, including DNAPL, from the subsurface at several sites. Cost information is very site-specific, depending on the amount and size of the particular array and length of operation.

This technology is best applied in small-diameter arrays, usually 30 feet. The six-phase heating could be used effectively in an area such as the Former Waste Disposal Area (FWDA) where space limitations exist. This technology also could be used in conjunction with other technologies to effectively remove NAPL and VOC contamination. This technology is one of the few proven technologies that work in soils with low permeability.

2.2 Dual-Phase Extraction or Bioslurping

2.2.1 Methodology

Dual-Phase Extraction involves installation of an extraction well equipped with an adjustable tube called a slurp tube. This technology is used predominantly for LNAPL recovery. The tube is connected to a vacuum pump so that the end of the tube is placed at the LNAPL level. The tube and vacuum extract LNAPL and limited amounts of groundwater according to the manufacturer. As the LNAPL level drops below the slurp tube, vapor extraction begins. As vapor is extracted, airflow is induced through the unsaturated zone and eventually the water level rises and the cycle begins again.

2.2.2 Evaluation of Dual-Phase Extraction or Bioslurping

This technology has been used for LNAPL removal successfully at several bulk storage facilities in the Northwest. Dual-Phase extraction is a relatively low-cost technology that requires minimal operation and maintenance (O&M) following installation. This technology could be more effective at LNAPL removal at the M&B site than the current passive skimmers installed at the site. In addition, the recovery of residuals in the vadose zone would be enhanced. Dual-phase wells could be installed independent of the vertical barrier or as part of another innovative technology at the site.

There are some inherent problems with dual phase wells. Increased aeration generated by vapor extraction can cause increased biofouling of well screens. Well screens may need to be treated and cleaned at yearly intervals to prevent biofouling.

2.3 Dynamic Underground Stripping

2.3.1 Methodology

DUS is a thermally enhanced in situ extraction technology that removes VOCs and semivolatile organic compounds, including NAPLs, from groundwater and soils above and below the water table. The DUS technology relies on three integrated technologies: electrical heating of clay and other lower-permeable soil layers, steam injection and vacuum extraction, and underground imaging using electrical resistance tomography to monitor and control the process.

DUS was developed through collaboration by researchers at the University of California at Berkeley and Lawrence Livermore National Laboratory.

2.4 Hydrous Pyrolysis Oxidation

HPO treatment is relatively simple and can be applied to large volumes of soil. Researchers have stated that the observed energy cost of heating soil to the boiling point by steam ($1.50 per cubic yard) makes it feasible to consider HPO as a potential large-volume cleanup technique.

HPO is an in situ thermal remediation technology that uses hot oxygenated groundwater to mineralize organic compounds, such as chlorinated solvents, and refractory hydrocarbons, such as creosote. HPO works on the principle that in the presence of oxidants (oxygenated water or soil minerals), chlorinated organic compounds will oxidize readily to carbon dioxide and chlorine ions when heated to the boiling point of water.

Today, the principal treatment method for chlorinated solvent- and polynuclear aromatic hydrocarbons contaminated soil is removal to landfills and incineration. HPO is a rapid, in situ remediation technique that destroys subsurface contaminants, such as DNAPLs, and dissolved organic compounds without the need for extraction. This technique injects steam and oxygen below the water table, building a heated, oxygenated zone in the subsurface. The heat and oxygen accelerate the rate of remediation compared to in situ bioremediation. HPO utilizes DUS to inject steam and oxygen into large volumes of subsurface soil.

2.4.1 Evaluation of Hydrous Pyrolysis Oxidation and DUS

HPO has been used successfully in conjunction with DUS (see Section 2.3) at a Superfund site in California. These technologies were used to treat creosote and pentachlorophenol (PCP) at depths 100 feet below ground surface. During the first six weeks of operation, approximately 300,000 pounds of contaminants was removed or destroyed in place.

Although these technologies have been very successful in removing DNAPL at wood-treating facilities, surface steam generation plants are required and can be expensive. Most of the sites that have documented success with these technologies had existing steam to the site. This would not be the case at the M&B site, because steam would need to be manufactured for the injection process.

DUS is best applied in conjunction with HPO at sites contaminated with PCP and creosote. This technology is best applied at sites with contaminants above and below the water table and at complex sites that are very difficult to clean up. DOE indicated DUS is a labor-intensive technology and requires significant field expertise to implement. The manufacturer recommends a full-time boiler operator to run the steam plant 24 hours per day and several field personnel, including field engineers, geophysicist and chemists.

However, this technology has been successful at sites similar to M&B. A power plant can be brought on site in a skid-mounted unit to manufacture steam. Power requirements for the system can be problematic, but not impossible to implement. A three-phase transformer would be needed to convert line power and deliver up to 300 amps per electrode.

The technology is licensed to SteamTech, Inc., and Integrated Water Technologies, Inc. Documented costs associated with this type of remediation have ranged from $25 to $75 per cubic yard, depending on the site.

2.5 In Situ Flushing

2.5.1 Methodology

Soil flushing is a commercially available, in situ technology for the treatment of soils contaminated with inorganic and organic compounds. The addition of compatible surfactants may increase the effective solubility of some organic compounds; however, the flushing solution may alter the physical and chemical properties of the soil system.

In situ soil flushing is the extraction of contaminants from soil with water or other suitable aqueous solutions. Soil flushing is accomplished by passing the extraction fluid through in-place soil using an injection or infiltration process. In most cases, extraction fluids must be recovered from the aquifer, and when possible, they should be recycled.

Surfactants may be added to increase the effective solubility of some organic compounds. The separation of surfactants from recovered flushing fluid or reuse in the process is a major factor in the cost of soil flushing. Treatment of the recovered fluids may result in process sludges and residual solids, such as spent carbon and/or and spent ion exchange resin, which must be treated appropriately before disposal.

Treatability tests are required to determine the feasibility of the specific soil flushing process being considered. Soil and contaminant characteristics will determine the flushing fluids required, flushing fluid compatibility, and changes in flushing fluids with changes in contaminants.

2.5.2 Evaluation of In Situ Flushing

Several surfactant flushing pilot studies have been performed at wood-treating facilities. Soil flushing was used to recover oil and to remove creosote contamination at the Laramie Tie Plant in Laramie, Wyoming. The initial level of total extractable organics was 93,000 parts per million (ppm), and after treatment the level was reduced to 4,000 ppm.

The major limitation of this technology is flushing of soils with low permeability. These soils are difficult to treat because surfactants can adhere or sorb to soil and reduce effective soil porosity. Reactions of flushing fluids also can reduce contaminant mobility. The potential of washing the contaminant beyond the capture zone and the introduction of surfactants to the subsurface may be a concern. This technology should be used only where flushed contaminants and soil flushing can be contained and recaptured. In addition, recovered groundwater and flushing fluids with the desorbed contaminants may need treatment to meet appropriate discharge standards.

This technology may be a good candidate for the M&B site following installation of a vertical barrier to contain surfactants and flushed contaminants. Site characteristics such as soil properties and groundwater depth make this technology a viable candidate for the M&B site.

2.6 Waterflood Oil Recovery

2.6.1 Methodology

Waterflood oil recovery is a commercially available, in situ technology for the treatment of groundwater contaminated with DNAPLs. Waterflood oil recovery is tailored to specific site conditions and generally is used in conjunction with barrier technologies.

The objective of waterflood oil recovery is to recover mobile NAPL and to mitigate potential further NAPL migration along select bedding planes. In full-scale application of waterflood DNAPL recovery, a module is created by constructing multiple sets of delivery and dual-recovery drain lines adjacently in an area containing mobile DNAPL. Delivery lines carry produced water to the lower boundary of the DNAPL. This enhances the hydraulic gradient and drives the mobile NAPL inward to the drain lines. With minor exceptions, little or no DNAPL is produced from the upper drain line.

Each unit within each module is operated until DNAPL recovery rates indicate that most of the DNAPL has been recovered. Recovery data from pilot and full-scale DNAPL recovery operations have indicated high initial recovery rates that gradually decrease with time.

2.6.2 Evaluation of Waterflood Oil Recovery

This technology has been used successfully in pilot-scale studies at former wood-treating facilities in the United States. A small-scale pilot system was installed successfully in Laramie, Wyoming. Site contaminants were similar to those identified at the M&B site. The Laramie site has lighter-than-water nonaqueous phase liquids (LNAPL) and DNAPL in groundwater beneath the site. The installed unit recovered 39,000 liters (L) of DNAPL in 30 days. A large-scale system also was installed successfully at the same site. A total of 870,000 L of DNAPL was recovered in 90 days.

Waterflood oil recovery is a favorable technology because it is used in conjunction with barrier wall systems. Cost specifications for this technology are not available. According to the vendor, water supply constitutes the main cost of the system. A cost analysis for this technology should be available in February 2000. Depending on the costs, the Waterflood oil recovery method of NAPL recovery should be considered for the M&B site following installation of a vertical barrier.

2.7 Hydrogen Peroxide In Situ Bioremediation

2.7.1 Methodology

Hydrogen peroxide-induced biodegradation involves introduction of oxygen-amended water to a contaminated subsurface environment via an injection well infiltration gallery (trench). Insufficient amounts of oxygen will limit the ability of microorganisms to degrade contaminants. Hydrogen peroxide generates oxygen as it decomposes, supplying the necessary aerobic environment for biodegradation. Nutrients, such as nitrogen and phosphorous, also may be added in the process to supplement microbial metabolic processes.

Decomposition of hydrogen peroxide may be catalyzed by iron; by fluctuations in solution pH; or by microbial enzymes, such as hydroperoxidases, catalases, or peroxidases. Catalase, found in almost all aerobic bacteria, is mainly responsible for catalytically decomposing hydrogen peroxide.

2.7.2 Evaluation of Hydrogen Peroxide In Situ Bioremediation

Hydrogen peroxide injection is a relatively simple technology that could be used at the M&B site. Site conditions (e.g., permeability and depth to groundwater) are favorable to hydrogen peroxide injection. The technology has been used in pilot-scale studies at some sites in the United States. However, the technology has several limitations and drawbacks. In situ biodegradation is limited by the rate at which oxygen is transferred to the contaminant-degrading microorganisms. Hydrogen peroxide is considered a cheap oxygen source because its decomposition generates oxygen. Thus, the use of hydrogen peroxide is predicated on its conversion to oxygen and water, and the rate of this conversion is critical to the successful use of hydrogen peroxide. Uncontrolled decomposition can result in supersaturation of water with oxygen, which can cause gas blockage and reduce permeability around injection points. In addition, there is potential for biotoxic concentrations of hydrogen peroxide in the groundwater.

Another limitation of using hydrogen peroxide as a bioremediation technique is its cost comparised to other technologies that are designed to provide aerobic environmental biodegradation. Hydrogen peroxide ranges from approximately $2.81 to $4.63 per kilogram of oxygen supplied. Because of this high cost and uncontrolled decomposition of the loss of oxygen equivalents are serious concerns. Because hydrogen peroxide is potentially toxic to microorganisms, the correct concentration is crucial.

Based on the limitations and lack of successful pilot-scale studies at wood-treating facilities, this technology would require bench-scale testing prior to implementation at the M&B site.

2.8 Membrane Filtration System

2.8.1 Methodology

The membrane filtration system removes and concentrates contaminants by pumping contaminated liquids through porous stainless steel tubes coated with specifically formulated membranes. Contaminants are collected inside the tube membrane, while clean water permeates the membrane and tubes. The concentrated contaminants are collected in a holding tank and fed to a treatment system such as the SBP Technologies, Inc. Bioremediation System. The relatively clean resulting water is referred to as "permeate", while the mass of contaminants trapped by the membrane is called "concentrate".

Integrating membrane filtration with SBP's bioremediation system allows removal and destruction of many contaminants, especially wood-preserving wastes and solvents. For waste-waters or slurries contaminated with inorganics or materials not easily bioremediated, the membrane filtration system can separate the material for treatment by another process. The system may be most suitable to treating relatively diluted but toxic waste streams, in which the percent reduction of contaminants will allow discharge of the permeate without further treatment. This feature makes the unit highly suitable for polishing effluents as part of a multi-technology treatment train.

The SBP hyperfiltration system has several unique features that provide advantages over the conventional membrane process in wastewater treatment applications. SBP uses proprietary formed-in-place membrane technology. The membrane is formed on porous sintered stainless steel tubes by depositing microscopic layers of inorganic and polymeric chemicals. The physical properties of the membrane can be varied by, controlling the type of membrane chemicals used, their thickness, and the number of layers. The formed-in-place membrane can be quickly reformulated economically in the field to accommodate changes in waste characteristics or treatment requirements.

A major limitation of many membrane systems is their propensity to irreversibly foul. Fouling is the buildup of materials on the surface of the membrane, leading to a loss of flux and eventual cessation of flow. SBP uses a cross-flow filtration mechanism to continuously clean the surface of the membrane, minimizing fouling. The feed stream is directed parallel to the membrane's surface, resulting in a cleaning action that minimizes buildup of materials on the membrane surface. Because all membranes eventually foul, a cleaning cycle is necessary to restore flux and operability. The formed-in-place membrane is compatible with many chemical cleaning methods. If the membrane should become irreversibly fouled, it can be stripped and reformulated on site.

2.8.2 Evaluation of Membrane Filtration System

This technology has been used with some success in pilot-scale studies at former wood-treating facilities similar to M&B. As previously discussed, the major limitation of this technology is fouling of the membrane. The pilot-scale studies have indicated that the SBP hyperfiltration method reduces fouling by 75%. However, some pretreatment may be necessary to remove free oil or suspended solids from the aqueous waste stream before membrane filtration. The cost of O&M is relatively low once the system is running. Documented pilot-scale studies have pumped water through the system from 7 gallons per minute (gpm) to 24 gpm. At a United States Environmental Protection Agency (USEPA) SITE demonstration at a wood-treatment facility, the SBP membrane filtration system effectively removed high molecular-weight compounds from the feed stream. This technology could be used in conjunction with a vertical barrier wall to actively remove NAPL at the M&B site.

Table 1

Summary of Enhanced NAPL Recovery Technologies

Technology	Brief Description	Advantages	Disadvantages	Order-of-Magnitude Costs
2. Established Technologies				
2.1: Six-Phase Soil Heating	Six-phase soil heating involves insertion of seven electrodes into the ground. These electrodes are installed in a hexagonal pattern with the seventh neutral electrode placed in the center of the pattern. Each electrode operates on a different phase, which is produced by a six-phase transformer that converts the standard three-phase electricity into six-phase electricity. The frequency resistively heats up the soil and creates steam via soil moisture. The electrodes serve as soil vapor extractors as the steam that is produced strips contaminants from the soil. A blower is used to extracted vapor from the soil. The vapor is run through a condenser, and liquids that result are treated with an air stripper.	SPH provides rapid method of cleanup and has the ability to function in low permeability soil. Greater degree of recovery. May be an effective technology used in conjunction with other remedial technologies at M&B.	Voltage used for remediation may cause grounding problems with electrical equipment on site. Health and safety concerns with voltage being applied to soil. Limitations on size of hexagonal pattern best results with diameter less than 30 feet.	Costs are very site-specific, depending on contaminants, area, and available utilities. Vendor would require site-specific needs before issuing a quote.
2.2: Dual-Phase Extraction or Bioslurping	DPE is an extraction well in which an adjustable slurp tube is installed. The tube is connected to a vacuum pump, and the end is placed at the LNAPL level. This tube extracts free product and some groundwater. When the LNAPL level declines in response to pumping, the slurp tube begins vapor extraction. As vapor is extracted, airflow is induced through the unsaturated zone and eventually the water level rises and the cycle begins again.	Less groundwater removed. Lower treatment cost. Smearing due to reduction in water level fluctuations. Recovery of residuals in the vadose zone enhanced. Low cost to maintain once installed. Can be utilized independently of other technologies.	Biofouling of well screen may occur because of active aeration. Lack of treatment of saturated zone.	Initial startup cost of installation of wells and vapor extraction. Cost would depend on the number of wells and the size of the vapor extraction system.
2.3: Dynamic Underground Stripping	Dynamic underground stripping (DUS) is a technique that combines technologies, previously used separately, to remediate a site. Steam injection and electrical heating are used in conjunction with a heat permeable and less permeable subsurface layer. Underground imaging tracks steam fronts to determine efficiency and placement of steam injection and extraction wells. Hydrous pyrolysis oxidation is a technique that is used in the process for in situ destruction of contaminate and enhanced bioremediation.	Highly effective for removing volatile and semi-volatile compounds. LNAPL and DNAPL are removed. Excellent process control, and very adaptive. Relatively inexpensive, and cleanup-up times are reduced from decades to years.	Initial startup costs are higher than pump and treat. Possible negative interaction between . equipment used for different techniques.	Not available.